Remarks

Claims 1 to 18 are pending. All of the pending claims have been rejected. Applicants address each of the Examiner rejections below. Applicants respectfully request reconsideration of the claims.

§ 112 Rejections

Claims 1-18 stand rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicant regards (or Applicants regard) as the invention. Applicants respectfully traverse this rejection.

With respect to claims 1, 17, and 18, the Examiner asserts that the language "with or without an intermediate layer" is unduly vague and indefinite with respect to what layers may or may not be present. Applicants submit that this language clearly indicates that the intermediate layer is an optional component. It may be present, but the claims do not require it to be. One of skill in the art would understand that the intermediate layer may be included if so desired, but it is not necessary. The rejection of these claims for indefiniteness should, therefore, be withdrawn.

With respect to the dependent claims, starting with claim 4 and continuing thereon, the Examiner asserts that a significant number of claims may be de facto duplicate claims. However, the Examiner will note that although claim 5-7 all recite the same limitation, each of these claims depends from a different base claim. The same is true of claims 8-10 and 12-16. Thus, all of the dependent claims are different in scope and are not duplicative.

Applicants submit that the rejection of claims 1-18 under 35 U.S.C. § 112, second paragraph, has been overcome, and that the rejection should be withdrawn.

§ 102 Rejections

Claims 1-7 stand rejected under 35 U.S.C. § 102(b) as being anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over Japanese Patent Showa (49-29613). Applicants respectfully traverse this rejection.

The Examiners states that Showa discloses the preparation of a pressure sensitive adhesive coated onto a suitable backing, such as tetrafluoroethylene, which is irradiated with a suitable

ionization radiation beam whereby the anchoring force of the adhesive agent relative to the substrate material is greatly improved. The Examiner asserts that this disclosure expressly provides all of the elements of claim 1, and inherently provides the limitations of claims 2-7, or that such limitations would be obvious. Applicants disagree.

Claim 1 is directed to a pressure sensitive adhesive sheet that includes a substrate "which is an electron-beam non-decaying fluorine-containing material sheet." Although tetrafluoroethylene is a fluorine-containing material, it is not "non-decaying" when irradiated with an electron-beam. As supporting evidence, Applicants direct the Examiner's attention to the data for Comparative Example 18, on page 32 of the present specification. Comparative Example 18 utilized polytetrafluoroethylene (PTFE) as a substrate, poly(α-olefin) as a PSA, and was separately cured via EB and via drying. When cured with EB, breakage was observed between the PTFE and the PSA and the tensile strength of the PTFE was deteriorated. Such effects were not observed when cured via drying. This supports Applicants' position that tetrafluoroethylene is not "non-decaying" when exposed to an e-beam.

As further evidence that tetrafluoroethylene decays upon exposure to an e-beam, Applicants submit herewith an article by Timmerman, *et al.*, Journal of Applied Polymer Science VI(22):456-460 (1962) (attached hereto as Exhibit A). On page 456, Timmerman et al state:

> Many reports have been received in the past regarding the radiation degradation of polytetrafluoroethylene.... [R]eferences give a compilation of data, all of which tend to show that polytetrafluoroethylene undergoes degradation when irradiated.... In general, it is found that, when polytetrafluoroethylene is irradiated, tensile strength decreases, elongation decreases, and density increases.

Indeed, the original intent of the study by Timmerman et al. had been to compare PTFE films that had been irradiated under different environmental conditions, but the initial results had been so discouraging that the investigators were led to experiment with other fluorinated polymers. Thus, by Timmmerman's own account, and by the accounts of other investigators identified by Timmerman, it is clear that PTFE undergoes substantial decay when irradiated with an e-beam.

As demonstrated above, Showa does not disclose a fluorine-containing substrate material that is "electron-beam non-decaying" as recited in claim 1. Showa, therefore, fails to provide, expressly or inherently, all of the limitations of claim 1, or dependent claims 2-7.

The rejection of claims 1-7 under 35 U.S.C. § 102(b) as being anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over Japanese Patent Showa (49-29613) has been overcome and should be withdrawn.

§ 103 Rejections

Claims 8-18 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Japanese Patent Showa (No. 49-29613). The Examiner relies on Showa for substantially the same reasons as provided above in connection with the rejection of claims 1-17. The Examiner further asserts that the features added by claims 8-18, e.g. to make the claimed sheet transparent or alternatively to use it as a protective sheet, are well within the ordinary skill of the art. Applicants respectfully traverse this rejection.

As discussed in detail above, Showa fails to teach or suggest use of a fluorine-containing substrate that is "electron-beam non-decaying" as recited in the claim 1. It is well-established that the fluorine-containing substrate identified by Showa, i.e. tetrafluoroethylene, undergoes substantial decay when exposed to an e-beam. Thus, even if the additional elements of claims 8-18 would have been obvious as the Examiner asserts, Showa nevertheless fails to provide all of the elements of the claimed invention.

The rejection of claims 8-18 under 35 U.S.C. § 103(a) as being unpatentable over Showa has been overcome and should be withdrawn.

Conclusion

In view of the foregoing amendments and remarks, Applicants respectfully submit that the application is in condition for allowance. Reconsideration of the application is requested.

All communications in this case should be direct to the undersigned. If the Examiner believes a telephone discussion would be helpful to resolve any of the outstanding issue in this case, the Examiner is encouraged to call the undersigned at the number listed below.

Respectfully submitted,

November 4, 2003
Date

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The Predominant Reaction of Some Fluorinated Polymers to Ionizing Radiation

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Many reports have been received in the past regarding the radiation degradation of polytetrafluoroethylene. Nishioka,[1] et al. found a decrease in melt viscosity, elasticity, and creep fracture time. Density and crystallinity increases supported the fact that the predominant reaction of polytetrafluoroethylene to ionizing radiation resulted in chain scission. Other references[2,3] give a compilation of data, all of which tend to show that polytetrafluoroethylene undergoes degradation when irradiated, that chain scission predominates over any crosslinking that may take place, and that the structural properties of the plastic are decreased. In general, it is found that, when polytetrafluoroethylene is irradiated, tensile strength decreases, elongation decreases, and density increases.

The original intent of this study was to compare polytetrafluoroethylene films that had been irradiated under various environmental conditions. It was desired to find a condition or conditions under which the degradation of polytetrafluoroethylene by irradiation could be minimized or by which crosslinking could be induced. Wall[4] reported that in the absence of oxygen polytetrafluoroethylene retained 51% of its original tensile strength whereas the same dose of radiation applied in air caused the sample to become so brittle that it could not be tested for tensile strength.

The environmental conditions, which were varied in the present experiment, included irradiations *in vacuo*, at elevated temperatures, in a nonoxygen atmosphere, and with combinations of these conditions. The rather discouraging results found with polytetrafluoroethylene led to the evaluation of the two other fluorinated polymers, polyvinylidene fluoride and polyvinyl fluoride. Both polymers have high melting properties and a heat resistance approaching, but not equal to, that of polytetrafluoroethylene. It was felt that the presence of hydrogen atoms along the polymer molecules might tend to cause crosslinking of these polymers or at least decrease the rate of degradation. These polymers were studied with the object of comparing radiation resistance with polytetrafluoroethylene. Heat aging tests are reported as a by-product of the radiation resistance studies.

EXPERIMENTAL PROCEDURES

All polytetrafluoroethylene samples tested were 0.010 in. thick, the polyvinylidene fluoride pellets were prepared into slabs 0.035 in. thick, and sheets of polyvinyl fluoride 0.003 in. thick were used. Samples were irradiated by passing them through the electron beam perpendicular to the axis of the beam. The geometry of the electron beam remained constant. The speed of passage through the beam and the point of entry into the beam were also constant. Radiation dose was varied either by varying the strength of the electron beam or by varying the number of passes through the beam that a sample would receive. Either method would be used, at the discretion of the operator, since the study was based on total dose and not on dose rate. Samples irradiated at elevated temperatures or in an atmosphere other than air or both were placed in a sealed rectangular container with the front face made of 0.0015 in. aluminum. This container was fitted with a gas inlet on one side and a hot plate in the rear. In this container either a controlled atmosphere or heat could be applied to a sample as it passed through the beam. The samples irradiated in a vacuum were placed in a steel

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EXHIBIT A

cylinder fitted with a 0.002 in. titanium window. The samples were placed directly behind the window and the container was evacuated to 30 μ of mercury before being passed through the electron beam. All polyvinyl fluoride and polyvinylidene fluoride samples were irradiated in air at room temperature. Dosimetry was accomplished with the use of an evacuated Faraday cage.

The cage was passed through the electron beam and dose was determined as a function of current through the Faraday cage. The irradiations were accomplished by using a Model EA-1.0 Dynamitron Electron Accelerator (from Radiation Dynamics, Inc.).

TESTING PROCEDURES

Tensile strength and elongation measurements were made on a Dillon tensile strength tester. Tests on this machine were performed in triplicate and results reported as an average value. Density determinations were made with the use of flotation methods. One determination was made on each sample tested. The cut-through test was performed by draping a sample over a mandrel in an oven. Weights were placed on the strips so that each strip held 15 lb./in.^{2} Maximum temperature attained was 255°C. Results of this test are presented in length of time for the strip to break and oven temperature at the time of break. The deformation under load test was performed by suspending 2 by 1 in. strips of polyvinylidene fluoride in an oven with 250-g. weight attached. Oven temperature was preset to 200°C. With an Ames ovenproof deformation test micrometer, the thickness of strips was determined when they were placed in the oven and then after 1 hr. in the oven. Results are expressed in per cent of original thickness retained by the sample. All tests were performed at least 24 hr. after irradiation, to allow time for delayed free-radical reaction, annealing of initial reaction, or escape of gases formed by diffusion.

RESULTS OF TESTS AND DISCUSSION

Table I shows the results of physical tests performed on polytetrafluoroethylene samples irradiated to 2–8 Mrad in oxygen and nonoxygen atmospheres. It is obvious from the results that the polytetrafluoroethylene samples in every case were degraded by ionizing radiation. Degree of degradation varied according to the conditions of irradiation; however, even the most favorable of conditions (irradiation in a vacuum) still resulted in relatively severe degradation. This sample lost 44.6% in tensile strength and 66.7% in elongation. This severe decrease in physical properties virtually eliminates polytetrafluoroethylene as a radiation-resistant plastic under the conditions tested. It is also evident from this figure that density of the plastic increased with increasing radiation. The detection of unsaturation[5] and the production of CF_4 gas[6] when polytetrafluoroethylene was irradiated indicate that density should decrease, since the ratio of fluorine to carbon decreased as radiation dose increased. Figure 1 shows changes in density in polytetrafluoroethylene with increasing dose of radiation under various environmental conditions. Densities could not be measured beyond 8 Mrad on any sample other than the room temperature nitrogen irradiation, owing to embrittlement of the samples. It is interesting to note that the slopes of the curves of samples irradiated at elevated temperatures are more steep than room-temperature-irradiated samples. The results shown in Table I indicate that at low radiation doses and in the presence of air degradation is greater when radiation is conducted at elevated temperature. Density changes in polytetrafluoroethylene may also indicate degree of radiation degradation. Possibly molecular configuration is altered during radiation, causing the decreased density. Since density changes in polytetrafluoroethylene are a function of void content and degree of crystallinity, and these values were not determined, conclusions were not drawn as to the cause of the density changes. Further work is being done on this phase, to determine volume changes and density changes when polytetrafluoroethylene is irradiated. Zero strength time measurements have paralleled tensile and elongation decreases. It will be noted that Wall reports that a dose of 6.56 Mrad gamma radiation in vacuum decreases 49% the

TABLE I
Physical Properties of Irradiated Teflon in Various Environments

Radiation dose, Mrad	Atm.	Temp., °C.	Tensile strength lb./in.^{2}	Elongation, %	Density, g./cc.	Zero strength, time, sec.
0	Air	25	5200	565	2.142	48.0
2	Air	25	2740	40	2.150	14.8
2	N.	25	2647	183	2.162	15.6
2	Air	100	2130	21	2.177	10.2
2	Air	200	1313	6	2.205	TBTT
2	N.	38	2700	188	—	15.7
2	N.	100	2413	142	2.151	15.8
2	Vac.	25	2880	188	—	—
8	Air	25	TBTT	TBTT	2.161	TBTT
8	N.	25	2513	55	2.160	14.7
8	Air	100	1013	8	2.197	TBTT
8	N.	100	2440	27	2.178	14.05
8	Vac.	25	2470	125	—	—

TBTT, too brittle to test.

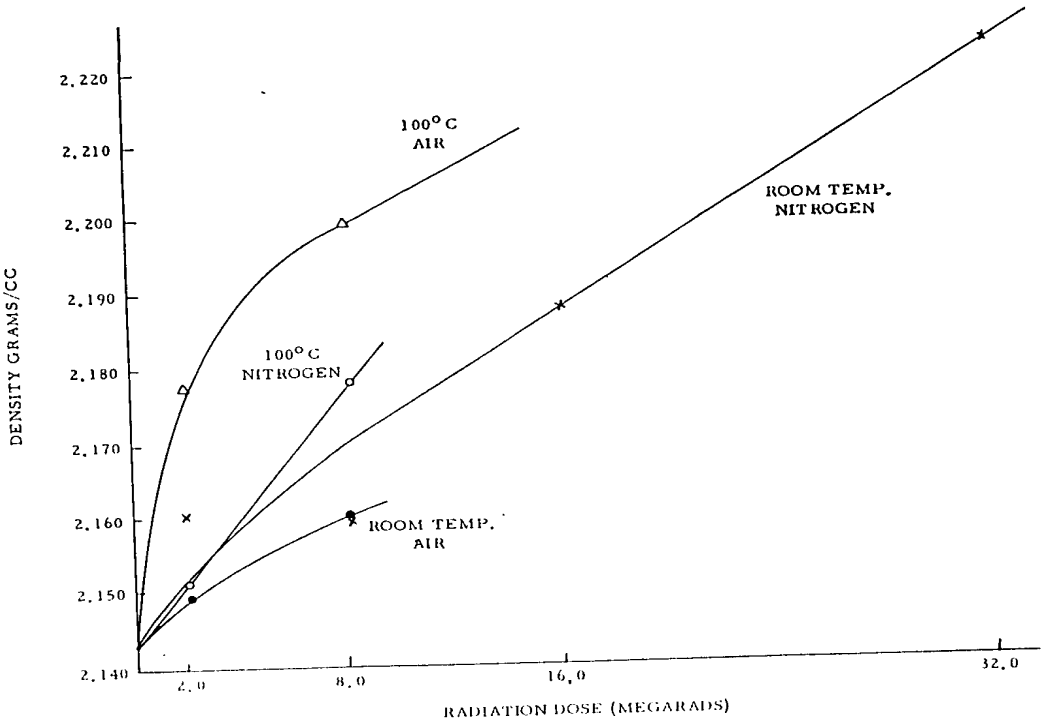

Fig. 1. Density changes in Teflon irradiated under different environmental conditions.

tensile strength of polytetrafluoroethylene. At 2 Mrad the evacuated sample in this test lost 44% tensile strength and at 8 Mrad the strip lost 52.5% tensile strength. This is an indication that this degradation in vacuum is independent of type of radiation and dose rate.

Figure 2 shows the changes in tensile strength and per cent elongation of irradiated polyvinyl fluoride and polyvinylidene fluoride samples, and deformation under load of irradiated polyvinylidene fluoride. Sample thickness of polyvinyl fluoride was not great enough to perform the deformation under load test. These results show that neither polymer is degraded in structural properties, by radiation, to the extent that polytetrafluoroethylene is degraded. Polyvinylidene fluoride is reported to have the structure $(—CH_2—CF_2—)_n$ and should be expected to degrade if compared with polyvinylidene chloride, a polymer known to undergo decreases in structural properties when irradiated. Even at the dose of 100 Mrad the polymer has a tensile strength greater than its tensile strength before radiation. This, coupled with the fact that elongation decreased with increasing dose, indicates that the polymer is crosslinked when irradiated. The deformation under load curve also indicates crosslinking. The tensile strength and elongation curves of polyvinyl fluoride, on the other hand, show degradation as dose is increased. However, the rate of degradation is much less than that of polytetrafluoroethylene. At a 100-Mrad dose of radiation the polyvinyl fluoride sample has lost virtually all its structural properties. Density values of irradiated polyvinylidene fluoride showed an initial sharp decrease at 2 Mrad followed by a continuous slow reduction. Polyvinyl fluoride, on the other hand, showed an initial increase in density at 2 Mrad followed by a return to its original density at 8 Mrad. Its density remains at its original density at 32 Mrad. It appears that polyvinylidene fluoride could replace Teflon for use in a radiation field. To confirm this, the cut-through test was performed. It was found that in this test, at elevated temperatures, irradiated polyvinyl fluoride was superior to both irradiated polytetrafluoroethylene and polyvinylidene fluoride. Table II shows the results of this test. The results must be considered with differences of the cross-sectional area of each strip in mind. Duplicate samples are reported, to indicate the consistency of results. Samples were hung at random throughout the oven, to allow for temperature differences within the oven. Since the loads per cross-sectional area of each strip were equal, the cut-through test was considered a better indication of the relative heat

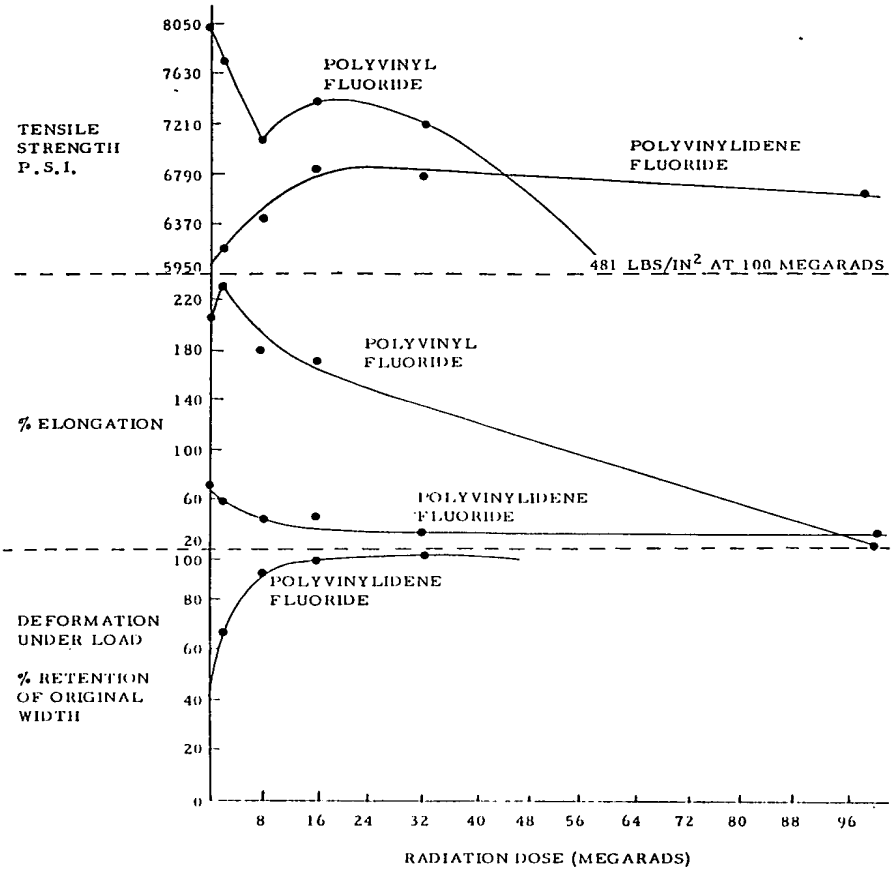

Fig. 2. Physical changes in irradiated polyvinyl fluoride and polyvinylidene fluoride.

resistance of the three polymers tested. Results indicate that unirradiated polytetrafluoroethylene has the greatest heat resistance of the samples tested. No breakage or embrittlement occurred at any time during the test. Polytetrafluoroethylene irradiated at 2 and 4 Mrad were cut through relatively fast and showed extreme brittleness when removed from the oven. These samples crumbled when handled. Polyvinylidene fluoride cut-through at lower temperatures and faster even than the irradiated polytetrafluoroethylene. The effect of radiation on the cut-through of polyvinylidene fluoride indicates a maximum value in time–temperature performance at 8 Mrad. All samples darkened during heat treatment and became quite brittle. In general, the performance in the cut-through test was inferior to that of polytetrafluoroethylene. On the other hand, irradiated and unirradiated polyvinyl fluoride showed no cut-through during the test. The samples were the only substances that had been irradiated and did not cut through during the entire test. Discoloration occurred slowly throughout the

TABLE II
Comparative Heat Aging Test on Irradiated Teflon, Polyvinyl Fluoride, and Polyvinylidene Fluoride

Plastic	Radiation dose, Mrad	Cross-section area, in.²	Wt. added, g.	Equiv. lb./in.²	Cut-through time, min.	Oven at break, °C.	See note
Teflon	0	0.0025	18.7	15	735	255	1
"	0	0.0025	18.7	15	735	255	1
"	2	0.0025	18.7	15	55	255	2
"	2	0.0025	18.7	15	55	255	2
"	4	0.0025	18.7	15	43	240	2
"	4	0.0025	18.7	15	55	255	2
Polyvinylidene fluoride	0	0.00875	60.0	15	18	200	3
"	0	0.00875	60.0	15	18	200	3
"	8	0.00875	60.0	15	27	230	3
"	8	0.00875	60.0	15	27	230	3
"	32	0.00875	60.0	15	20	206	3
"	32	0.00875	60.0	15	20	206	3
Polyvinyl fluoride	0	0.0015	10.2	15	735	255	3
"	0	0.0015	10.2	15	735	255	3
"	8	0.0015	10.2	15	735	255	3
"	8	0.0015	10.2	15	735	255	3
"	32	0.0015	10.2	15	735	255	3
"	32	0.0015	10.2	15	735	255	3

1411 samples irradiated in air at room temperature.
Note 1. No embrittlement noticed.
Note 2. Samples embrittled, no discoloration.
Note 3. Samples embrittled and browned.

test. It was interesting to note that the polyvinyl fluoride samples contracted during heating. Apparently, the 3-mil film had been stretch-oriented. The unirradiated samples decreased in longitudinal dimension about 50%. The 8-Mrad samples contracted about 20%, while the 32-Mrad samples showed no appreciable contraction. This strongly suggests that crosslinking had taken place during the radiation treatment of the samples. Although the irradiated polyvinyl fluoride samples withstood the cut-through test better than did the polytetrafluoroethylene samples, the latter were embrittled during heat testing. The finished sample did not crumble in the hand as did irradiated polytetrafluoroethylene, but could be flex-cracked quite easily. At the test temperature, irradiated polyvinyl fluoride was far superior in cut-through to irradiated polytetrafluoroethylene.

The authors are indebted to the Du Pont Company for polyvinyl fluoride samples, to Pennsalt Chemical Company for polyvinylidene fluoride samples, to Hitemp Wires, Inc., for preparation of polytetrafluoroethylene samples and for permission to publish, and to Radiation Dynamics, Inc., for use of the Dynamitron electron accelerator and permission to publish.

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Synopsis

Polytetrafluoroethylene was irradiated in air, in a vacuum, at elevated temperature, in a nitrogen atmosphere, and in some combinations of these conditions. In all cases the plastic was found to degrade in its structural characteristics. Even the most favorable condition of irradiation (irradiation *in vacuo*) resulted in a 44% reduction of tensile strength at a dose of 2 Mrad. Polyvinylidene fluoride resisted radiation to at least 100 Mrad effectively. Polyvinyl fluoride was structurally degraded at this dose but retained its structural properties to at least 32 Mrad A cut-through test under heat, comparing polytetrafluoroethylene with polyvinylidene fluoride and polyvinyl fluoride, showed: (*a*) Unirradiated polytetrafluoroethylene was most resistant to heat aging. (*b*) Irradiated and unirradiated polyvinylidene fluoride was inferior to irradiated polytetrafluoroethylene in heat resistance. (*c*) Irradiated polyvinyl fluoride was superior to irradiated polytetrafluoroethylene; polytetrafluoroethylene at 2 Mrad was inferior to polyvinyl fluoride at 32 Mrad in cut-through testing. (*d*) Polyvinylidene fluoride irradiated and unirradiated and polyvinyl fluoride and irradiated polytetrafluoroethylene all embrittled during heat testing.

Résumé

On a irradié le polytétrafluoroéthylène dans l'air, sous vide, à température élevée, sous atmosphère d'azote et dans diverses combinaisons de ces conditions. Dans toutes les expériences, on a trouvé que le plastique se dégradait suivant ses caractéristiques de structure. Même dans les conditions les plus favorables (sous vide), l'irradiation avec une dose de 2 Mrads provoque une diminution de la résistance à la traction. Le fluorure de polyvinylidène résiste efficacement aux radiations même à des doses aussi élevées que 100 Mrads. Le fluorure de polyvinyle est dégradé structurellement à cette dose mais garde ses propriétés jusqu'à au moins 32 Mrads. Si on compare le fluorure de polytétrafluoroéthylène, la fluorure de polyvinylidène et le fluorure de polyvinyle par un essai d'incision on trouve que (*a*) le fluorure de polytétrafluoroéthylène non irradié est plus résistant à la chaleur, (*b*) que le fluorure de polyvinylidène irradié ou non a une résistance à la chaleur inférieure à celle du fluorure de polytétrafluoroéthylène irradié, (*c*) que le fluorure de polyvinyl irradié est supérieur au fluorure de polytétrafluoroéthylène irradié. Ce dernier irradié avec une dose de 2 Mrads est inférieur au premier irradié avec 32 Mrads du point de vue de l'essai par incision; (*d*) et que le fluorure de polyvinylidéne irradié, le fluorure de polyvinyle nonirradié et le polytétrafluoroéthylène devienment fragile par suit d'un traitement à la chaleur.

Zusammenfassung

Polytetrafluoroäthylen wurde in Luft, im Vakuum, bei erhöhter Temperatur, in einer Stickstoffatmosphäre und unter einigen Kombinationen dieser Bedingungen bestrahlt. In allen Fällen wurde in der Strukturcharakteristik ein Abbau des Polymeren gefunden. Sogar unter den günstigsten Bestrahlungsbedingungen (Bestrahlung im Vakuum) nahm die Zugfestigkeit bei einer Bestrahlungsdosis von 2 megarad um 44% ab. Polyvinylidenfluorid zeigte einen ausreichenden Widerstand gegen Bestrahlung bis 100 megarad. Polyvinylfluorid wurde bei dieser Bestrahlungsdosis strukturell abgebaut, behielt jedoch seine Struktureigenschaften bis zu 32 megarad. Anhand eines Durchschneidetests bei erhöhter Temperatur wurde Polytetrafluoräthylen mit Polyvinylidenfluorid und Polyvinylfluorid verglichen; dieser zeigte folgendes: (*a*) Unbestrahltes Polytetrafluoräthylen war gegen Hitzealterung am beständigsten; (*b*) bestrahltes und unbestrahltes Polyvinylidenfluorid waren gegen Hitze weniger beständig als bestrahltes Polytetrafluoräthylen; (*c*) bestrahltes Polyvinylfluoid war hitzebeständiger als bestrahltes Polytetrafluoräthylen. Polytetrafluoräthylen mit 2 megarad war im Durchschneidetest weniger beständig als Polyvinylfluorid mit 32 megarad. (*d*) Bestrahltes und unbestrahltes Polyvinylidenfluorid, Polyvinylfluorid und bestrahltes Polytetrafluoräthylen wurden während des Hitzetests spröde.

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